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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An investigation of the electronic excitation structure of the transition metal oxides was begun which included the effects of correlation of the excited electron with the surrounding medium, relaxation of the electrons around the hole left by the excitation, and the interaction of the excited electron with the hole. Recent theoretical and experimental work has shown that all these effects must be included in order to obtain a detailed understanding of the excitation structure, optical properties, (continued)

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lattice dynamics, and dielectric response of these oxides and many other materials. Local orbitals instead of the usual spatially extended Bloch representation were used. The local orbitals are especially useful in describing the d-electrons, which are localized in position and energy. The extensive codes necessary for the efficient calculation of multicenter integrals were constructed and assembled during the past year. The methods necessary for transforming the band states from the Bloch to the local orbitals representation were developed, and the methods for diagonalizing very large array were investigated.

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ANNUAL REPORT

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AFOSR 76-3108

THEORETICAL INVESTIGATION OF THE EXCITATION
STRUCTURE AND OPTICAL PROPERTIES OF TITANIUM,
VANADIUM, AND THEIR OXIDES

A. Research Objectives

We began with the following objectives:

- to investigate the electronic excitation structure of transition metal oxides

- to do the study in the framework of the local orbitals method.

During the past year we have pursued the following specific objectives:

- construction of calculational methods

- development of codes for efficient calculation of individual multicenter two electron integrals using Slater Type Orbitals

- development of codes for transforming the joint density of states information from a Bloch representation to a local orbitals representation

- development of codes for reordering the integrals into groupings describing particle-hole interactions

- beginning the development of methods for diagonalizing very large arrays to find the excitation spectra using an extension of the methods of degenerate perturbation theory.

B. Status of Research

B.1 Development of Calculation Methods

As we discussed in our original proposal, the excitation spectrum is contained in the poles of the particle-hole (PH) propagator $\underline{\Pi}(\omega)$. We may construct the PH propagator with the eigenvectors $\vec{C}(\omega)$ from the matrix equation, represented here schematically,

$$\underline{\Pi}(\omega)^{-1} \vec{C}(\omega) = \Lambda(\omega) \vec{C}(\omega) \tag{1}$$

with

$$\underline{\Pi}(\omega)^{-1} = \underline{\Pi}^{o}(\omega)^{-1} - \underline{K}(\omega) . \tag{2}$$

$$\Lambda(\omega^{m}_{ex}) = 0$$

The solutions ω^{m}_{ex} are the excitation energies which induce poles in $\underline{\Pi}(\omega)$.

The primary equation to be solved is Eq. (1) with the structure presented in Eq. (2). The matrix $\underline{\Pi}^{o}(\omega)^{-1}$ has the form

$$\Pi^{o}_{ss'}, {}^{\vec{q}}(\omega)^{-1} = \sum_{n_1 n_2 \vec{k}} T_s^{*}(n_1\vec{k}, n_2\vec{k}+\vec{q}) \chi^{0}(n_1\vec{k}, n_2\vec{k}+\vec{q};\omega)^{-1} T_{s'}\cdot(n_1\vec{k}, n_2\vec{k}+\vec{q}) \tag{3}$$

with

$$T_s(n_1\vec{k}, n_2\vec{k}+\vec{q}) = \frac{1}{N} \sum_{\ell\ell'} e_\ell(n_2\vec{k}+\vec{q})^{*} e_{\ell'}(n_1\vec{k}) \tag{4}$$

$$e^{i\vec{k}\cdot\vec{R}_a} \sum_{cd} S_{0\ \ell,cj} e^{i(\vec{k}+\vec{q})\cdot\vec{R}_c} S_{0\ i,\ d\ell'} e^{i\vec{k}\cdot\vec{R}_d}$$

$$s = \{ji;0a\}$$

where n_1 is the band index, $e_{\ell'}(n,\vec{k})$ is a coefficient in the local orbitals

expansion of the Bloch function and S is the overlap matrix between local orbitals. $\underline{\chi}^0(\omega)^{-1}$ is just the inverse of the polarizability for the non-interacting particle-hole pair, and it is given by

$$\chi^0(n_1\vec{k},n_2\vec{k}+\vec{q};\omega)^{-1} = f_{n_1\vec{k}}(1-f_{n_2\vec{k}+\vec{q}})\{\omega-E_{n_2\vec{k}+\vec{q}} + E_{n_1\vec{k}}\} \qquad (5)$$

$$- f_{n_2\vec{k}+\vec{q}}(1-f_{n_1\vec{k}})\{\omega+ E_{n_2\vec{k}+\vec{q}} - E_{n_1\vec{k}}\} ,$$

where $E_{n\vec{k}}$ and $f_{n\vec{k}}$ are the one-particle energy and occupation number for Bloch state $n\vec{k}$. It is the inverse of Eq. (3) that is normally used in place of $\underline{\Pi}(\omega)$ in Eq. (1) to calculate the optical absorption. The inclusion of $\underline{K}(\omega)$ in Eq. (1) introduces particle-hole interactions. The first-order expression for $\underline{K}(\omega)$ in terms of local orbitals is

$$K_{ss'} = V_{aibj,b'j'a'i'} - V_{aia'i'jb'j'bj} \qquad (6)$$

with

$$V_{aibj',a'i'b'j'} = <\phi_{ai}(\vec{r})\phi_{a'i'}(r') \; \frac{e^2}{|\vec{r}-\vec{r}'|} \; \phi_{bj}(\vec{r})\phi_{b'j'}(\vec{r}')>$$

Under certain assumptions, the one-particle energy band $E_{n\vec{k}}$ in Eq. (5) and the corresponding Bloch coefficients used to construct $T_s(n_1\vec{k},n_2\vec{k}+\vec{q})$ in Eq. (4) may be replaced by quantities which include correlation and relaxation. Basically, these assumptions are valid when the sturcture of the hole (or particle) is not affected much by the particle-hole interaction. We have done calculations on atomic systems which show that this simple inclusion of relaxation and correlation effects along with including the effect of the particle-hole interaction results in much improved excitation energies.[1] The work of Kunz et al on the optical absorption of LiF[2] suggests that in certain

cases such an inclusion of separate effects is valid for solids. Certainly such a separation of effects would be fruitful whenever it is suspected that an excitation results in a well-localized hole, as is the case for the d-bands in transition metals where calculations of the dielectric matrix have shown that local field effects are important.[3]

The solution of Eq. (2) using Eqs. (3-5) requires the diagonalization of a huge matrix. However, if our local orbitals basis is well chosen, only a few terms from that matrix are large for a given range of excitation energies. To obtain a method which will allow us to solve Eq. (2) in a manageable sub-space while retaining the ability to calculate the effects of terms not in the principle subspace, we have developed a variation on degenerate perturbation theory. Suppose the matrix $\underline{\Pi}(\omega)^{-1}$ is arranged as illustrated in Fig. 1. We have assumed the total matrix is of size Nm x Nm and have arranged the elements along the diagonal into N mxm blocks, $\underline{\Pi}_{11}^{-1}$ .... $\underline{\Pi}_{nn}^{-1}$. Then the eigenvalue problem becomes

$$(\Delta - \underline{\Pi}_{11}^{-1})\vec{C}_1 = \sum_{\mu \neq 1} \underline{\Pi}_{1\mu}^{-1} (\Delta - \underline{\Pi}^{-1})^{-1} \underline{\Pi}_{\mu 1} \vec{C}_1 \qquad (7)$$

$$+ \sum_{\mu \neq \nu \neq 1} \underline{\Pi}_{1\mu}^{-1} (\Delta - \underline{\Pi}_{\mu\mu}^{-1})^{-1} \underline{\Pi}_{\mu\nu}^{-1} (\Delta - \underline{\Pi}_{\nu\nu})^{-1} \underline{\Pi}_{1}^{-1} \vec{C}_1 + \dots ,$$

where Δ is a true eigenvalue of the total matrix and $\vec{C}_1$ is a projection of the total eigenvector on the subspace. The elements of $\underline{\Pi}^{-1}$ could be arranged in order of importance with respect to $\underline{\Pi}_{11}^{-1}$ so that, for example, $\underline{\Pi}_{12}^{-1}$ is larger than $\underline{\Pi}_{13}^{-1}$ and so on. In practice we expect the series in Eq. (7) to be rapidly convergent.

$$\underline{\pi}^{-1}\,\vec{c} = \begin{pmatrix} \underline{\pi}^{-1}_{11} & \underline{\pi}^{-1}_{12} & & & - & \underline{\pi}^{-1}_{1N} \\ \underline{\pi}^{-1}_{21} & \underline{\pi}^{-1}_{22} & & & & \\ & & & & & \\ & & & & & \\ \underline{\pi}^{-1}_{N1} & & & & & \underline{\pi}^{-1}_{NN} \end{pmatrix} \begin{pmatrix} \vec{c}_1 \\ \\ \\ \\ \vec{c}_N \end{pmatrix}$$
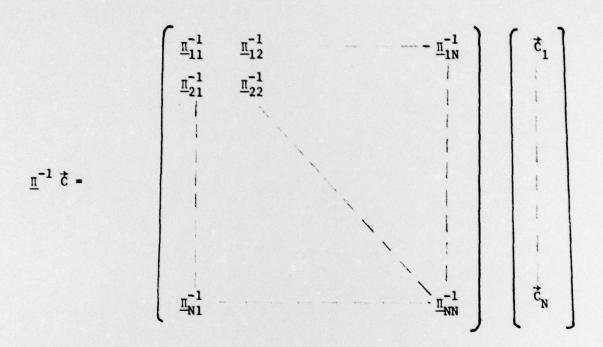
Figure 1.   Block Form for PH Propagator Matrix.

B.2 Calculation Program

During the first year of this research, we have made a good deal of progress toward setting up our program to calculate electronic excitation structure. One of the major tasks completed was the construction of computer codes to calculate general, multicenter two-electron integrals in an STO basis. We have also set up the necessary programs to transform and rotate our integrals between equivalent lattice sites. These programs are now running and are the only completely general programs for calculating two-electron integrals, actually without regard to basis type, of which we know. We need these general codes because, as is indicated in Eq. 6, the two-electron integrals do not involve just matrix elements between one-electron densities as is the case in energy band calculations. The electronic excitation problem involves two-electron density functions, and thus we need individual two-electron matrix elements. Fortunately we are helped by the nature of the local orbitals method. The method produces orbitals which are separated into independent subspaces over occupied and unoccupied bands. Since $\underline{\chi}_o^{-1}$ in Eq.(5) involves only occupied, unoccupied pairs of Bloch states, the local orbitals in Eqs. (3) and (5) occur only in occupied, unoccupied pairs, too. This property greatly reduces the size of our matrix problem.

We have also set up the necessary computer codes to calculate the inverse of the PH propagator given in Eq. (2). We use the method outlined in the last section. The Bloch sums involving the transformation matrix $\underline{T}_s$ in Eq. (4) are performed using the Lehman-Taut method. We have generalized this method to calculate efficiently Bloch sums over the entire Brillouin zone for all the combinations of bands. We can vary the number of shells of atoms included in the calculation, and the central matrix which we diagonalize contains only the

most important two-center, two-electron integrals for a given excitation energy. The three- and four-center integrals are included as needed in the perturbation expansion.

We have recently obtained good, self-consistent local orbitals energy band results for TiO calculated by Jennison and Kunz. These results were obtained with the local exchange approximation rather than with Hartree Fock exchange and thus have a gap between the p and d densities of states in agreement with the most recent photoemission measurements. Evidently the difference between Hartree Fock and local exchange is due to the inclusion of relaxation-correlation effects in the latter's energy bands. Thus our optical calculations automatically include some correlation effects.

We are also planning our calculations of the excitation structure in TiO. The optical spectra of several of the transition metal oxides show strong charge transfer structures just above the band edge in energy. The calculated d-bands for TiO are broader than, say, for NiO. However, since the final configuration is Ti^{++}, O^{--}, we expect charge transfer structure to exist in the TiO spectra. Ichikawa et al[5] have also compared the TiL_3 X-ray emission spectrum for TiO with the $M_{2,3}$ spectrum. The initial states responsible for the two spectra both have p symmetry and the final states are common. Then it is expected from the itinerant electron model that these spectra should show similar profiles. They do not, and, furthermore, the $M_{2,3}$ spectrum does not resemble the calculated density of states. These differences are evidently due to particle-hole interactions. We have an approach to calculate optical properties which includes particle-hole interactions and is based on local orbitals results which give good descriptions of ground state properties. Without such an approach, one cannot explain the above localized excitation

structures and, at the same time, explain the structure in the spectra due

to excitations of itinerant electrons between energy bands.

C. <u>References</u>

1. M. W. Ribarsky, Phys. Rev. A <u>12</u>, 1739 (1975).

2. A. B. Kunz, D. J. Mickish and T. C. Collins, Phys. Rev. Lett. <u>31</u>, 756 (1973).

3. W. Hanke and L. J. Sham, Phys. Rev. B <u>12</u>, 4501 (1975).

4. B. H. Brandow, Rev. Mod. Phys. <u>39</u>, 771 (1967).

5. K. Ichikawa, O. Terasaki, and T. Sagawa, J. Phys. Soc. Jap. <u>36</u>, 706 (1974).

D. <u>Professional Personnel</u>

The following individuals have participated in this research.

1. Dr. M. W. Ribarsky   Principal Investigator

2. Mr. David Luedtke   Graduate Student

E. <u>Papers and Presentations</u>

"Excitation Structure of TiO," M. W. Ribarsky, Bull. Am. Phys. Soc. <u>22</u>, 550 (1977).